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Determination of propoxur in environmental samples by automated solid-phase extraction followed by flow-injection analysis with tris(2,2′-bipyridyl)ruthenium(II) chemiluminescence detection

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Abstract

A sensitive method for the analysis of propoxur in environmental samples has been developed. It involves an automated solid-phase extraction (SPE) procedure using a Gilson Aspec XLi and flow-injection analysis (FI) with chemiluminescence (CL) detection. The FI–CL system relies on the photolysis of propoxur by irradiation using a low-pressure mercury lamp (main spectral line 254 nm). The resultant methylamine is subsequently detected by CL using tris(2,2′-bipyridyl)ruthenium(III), which is on-line generated by photo-oxidation of the ruthenium(II) complex in the presence of peroxydisulfate. The linear concentration range of application was 0.05–5 $\mu g\,mL^{-1}$ of propoxur, with a detection limit of 5 $ng\,mL^{-1}$. The repeatability was 0.82% expressed as relative standard deviation ($n = 10$) and the reproducibility, studied on 5 consecutive days, was 2.1%. The sample throughput was 160 injection per hour.

Propoxur residues below ng mL^{-1} levels could be determined in environmental water samples when an SPE preconcentration device was coupled on-line with the FI system. This SPE–FI–CL arrangement provides a detection limit as low as 5 $ng\,L^{-1}$ using only 500 mL of sample. In the analysis of fruits and vegetables, the detection limit was about 10 $\mu g\,kg^{-1}$.

Keywords: Propoxur; Tris(2,2′-bipyridyl)ruthenium(III) photogenerated; Flow-injection; Automated solid-phase extraction; Environmental samples

1. Introduction

Propoxur (*o*-isopropoxyphenyl *N*-methylcarbamate) is a non-systemic insecticide which is compatible with most insecticides and fungicides except alkalines. It is used on a variety of insect pests such as chewing and sucking insects, ants, cockroaches, crickets, flies and mosquitoes, and may be used for control of these in agricultural or in non-agricultural applications (e.g. private and public parks and gardens). Propoxur is available in several types of formulations and products, including emulsificable concentrates, wettable powders, baits, aerosols, fumigants and granules. Acute exposure of humans to propoxur by ingestion leads to the cholinesterase inhibition of red blood cells, with mild cholinergic symptoms including blurred vision, nausea, vomiting, sweating and tachycardia; however, these effects are transient. Due to its high solubility in water, propoxur is a potential contaminant of the aquatic environment and food sources. The permitted levels of residues of this insecticide are regulated by international organizations, for example, the European Drinking Water Directorate imposed a limit of 0.1 $ng\,mL^{-1}$.

A number of analytical methods for the determination of *N*-methylcarbamates pesticides in various matrices have been developed [1]. Spectrophotometric methods for the determination of propoxur are typically based on alkaline hydrolysis, followed by coupling of the resulting phenol derivative with different diazotised reagents [2–4] to produce strongly coloured species. High-performance liquid chromatography is the favoured technique since this insecticide lacks the thermal stability necessary for gas chromatographic determination. The most usual method for the determination of propoxur is based on fluorimetric detection, which implies a previous separation by liquid chromatography, a post-column basic hydrolysis for the production of methylamine followed by condensation with *o*-phtaldehyde and 2-mercaptoethanol to produce a highly fluorescent isoindole [5].

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In recent years, a series of procedures has been proposed for analysing *N*-methylcarbamate pesticides using the concepts of flow-injection analysis (FI) methodology [6–8]. Propoxur has been determined by FI procedures on the basis of its hydrolysis and coupling with *p*-aminophenol with spectrophotometric detection of the dye formed [9–11]. In another report, a procedure based on the inhibition of the cholinesterase activity was developed [12].

Chemiluminescence (CL) is becoming a powerful analytical tool for the determination of a large variety of analytes because of its low detection limit and wide linear dynamic range. The combination of FI and CL detection has made both techniques even more attractive because it is possible to mix samples and reagents with high reproducibility and improved sensitivity, selectivity and precision [13–15]. One of the most interesting CL reactions is that involving the oxidation of tris(2,2′-bypiridyl)ruthenium(II), $Ru(bipy)_3^{2+}$, to $Ru(bipy)_3^{3+}$ which is then followed by reduction with an analyte species with the subsequent emission of light [16–18].

A recent publication from our laboratory reported the CL detection of three *N*-methylcarbamate pesticides based on their photoconversion into methylamine, which subsequently reacted with $Ru(bipy)_3^{3+}$ [19,20]. The present investigation extends this work to the determination of propoxur. In our study, a completely automated method has been developed for first time for the FI determination of ultra trace quantities of this insecticide in environmental waters, vegetables and fruits using the combination of solid-phase extraction (SPE)–FI–CL detection. SPE is performed with the aid of the Aspec XLi, resulting in complete automation of cartridge conditioning, sample loading, cartridge air-drying, analyte elution, eluate-drying, sample reconstitution and sample injection steps.

2. Experimental

2.1. Reagents

All chemicals standards and reagents were of analytical grade. Ultrapure water from a Milli-Q plus system (Millipore-Ibérica, Madrid, Spain) was used. A stock standard solution was prepared by dissolving 50 mg of the product from Riedel-de Haën (Germany) in 25 mL of acetone and diluting to 500 mL with ultrapure water. This solution was stable for at least 2 months if stored in the dark at 4 °C. Solutions of lower concentration were freshly prepared by dilution of the stock solution with ultrapure water maintaining 5% (v/v) of acetone. An aqueous solution of 2×10^{-3} mol L^{-1} $Ru(bipy)_3^{2+}$ was prepared by dissolving an appropriate amount of $Ru(bipy)_3Cl_2 \cdot 6H_2O$ in ultrapure water.

2.2. Apparatus and manifold

The FI manifold used for the determination and CL detection of propoxur is a four-channel configuration working in the merging zone mode (Fig. 1). Two Gilson (Middleton, WI, USA) miniplus 3MP4 peristaltic pumps were used to deliver

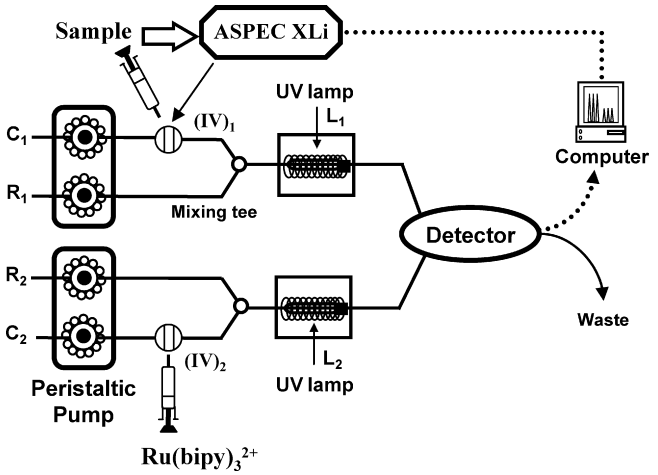

Fig. 1. Schematic diagram of the FI manifold. C_1 and C_2 = water; $R_1 = 0.05$ mol L^{-1} phosphate buffer of pH 6.5; $R_2 = 1.5 \times 10^{-3}$ mol L^{-1} potassium peroxydisulfate and 0.05 mol L^{-1} phosphate buffer of pH 5.7; $(IV)_1$ and $(IV)_2$ = injection valves; L_1 and L_2 = photoreactors.

the reagent streams through the flow system. The sample and the $Ru(bipy)_3^{2+}$ solutions were simultaneously injected in two carrier (water) streams with the aid of two Ommifit (Cambridge, UK) rotary valves. The carrier containing the sample was directed to the photoreactor L_1 (0.5 mm i.d., 200 cm length), where the photodegradation of propoxur to methylamine took place. The other carrier stream merged with the peroxydisulfate stream to achieve the oxidation of $Ru(bipy)_3^{2+}$ to $Ru(bipy)_3^{3+}$ along the photoreactor L_2 (0.5 mm i.d., 190 cm length). The subsequent confluence of the streams emerging from L_1 and L_2 reactors into the flow cell resulted in the emission of light. The CL emission was measured in a Camspec CL-2 (Cambridge, UK) luminometer connected to an Aminco Bowman (Thermospectronic, San José, CA, USA) Series 2 luminescence spectromer in order to use its software equipped with a data control and acquisition program.

The photoreactors consisted of PTFE tubing helically coiled around a rod-shape low-pressure mercury lamp (50 mm × 5 mm). The lamp operated at 8 W with a main spectral line at 254 nm. The excellent performance of PTFE at irradiation wavelengths below 300 nm is based on a diffuse radiation transfer and an internal reflectance (light tube) effect [21]. Each photoreactor was housed in a fan-ventilated metal box covered with mirrors to increase the photon flux. The tubing between the photoreactors and the flow cell was covered with black insulating tape to prevent a fibre optic effect from introducing stray light into the detector.

All extraction steps were performed automatically with the Aspec XLi (Gilson), which uses positive pressure elution to automate SPE with the added capability of injecting samples directly into the on-line FI system. The instrument was equipped with two bottles containing methanol and a mixture of dichloromethane–methanol (80:20, v/v), respectively. The separate reservoir solution was ultrapure water. The software used was a Gilson 735 Sampler Controller, which permits the system to be interfaced with the FI manifold.